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PRODUCTION OF CERAMIC PIGMENTS WITH DIOPSIDE STRUCTURE FROM TALC

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The results of investigation of synthesis of ceramic pigments with diopside structure are presented. Two reactions of diopside production are considered. It is indicated that the use of natural talc mineral makes it possible to lower the expense of pigment production and expand the pigment color range.

Production of ceramic pigments based on silicates is an important sector of contemporary research and development. The fundamental concepts of the synthesis of ceramic pigments are expanded, and the opportunities of using natural mineral materials arise, which makes it possible to decrease the synthesis temperature and to lower the cost of pigment production.

There are research data available on ceramic pigments with diopside structure obtained both from oxides [1] and from natural minerals (USSR inventor's certificate 1353787). There is reason for assuming that some other minerals containing calcium and(or) magnesium oxides can serve after additional charging as the basis for synthesis of ceramic pigments with diopside structure.

The authors of the present paper believe that talc is the best natural mineral for this purpose. Owing to the peculiarities of its crystal structure, talc produces on heating magnesium metasilicate and free silica [2]

$$3MgO \cdot 4SiO_2 \cdot H_2O = 3(MgO \cdot SiO_2) + SiO_2 + H_2O.$$

The chain structure of magnesium metasilicate is favorable for formation of the pyroxene structure of diopside with additional charging. Calcium and silicon oxides can be introduced through wollastonite adjusting the stoichiometric composition with calcium and magnesium oxides.

In the process of producing pigments with diopside structure from talc and wollastonite, two reactions were investigated:

$$3MgO \cdot 4SiO_2 \cdot H_2O + 2(CaO \cdot SiO_2) + CaO = 3(CaO \cdot MgO \cdot 2SiO_2) + H_2O; \quad (1)$$

$$3MgO \cdot 4SiO_2 \cdot H_2O + 4(CaO \cdot SiO_2) + MgO = 4(CaO \cdot MgO \cdot 2SiO_2) + H_2O. \quad (2)$$

In this case, substitution of chromophoric ions for magnesium and calcium ions should proceed according to the following pattern:

$$Mg_3(OH)_2[Si_4O_{10}] + 2CaSiO_3 + (1-x)CaO + xMeO = 3(Ca_{1-0.33x}Me_{0.33x}MgSi_2O_6) + H_2O;$$

$$Mg_3(OH)_2[Si_4O_{10}] + 4CaSiO_3 + (1-x)MgO + xMeO = 4(CaMg_{1-0.25x}Me_{0.25x}Si_2O_6) + H_2O,$$

where MeO are chromophoric metal oxides; the value of x in both reactions varies from 0 to 1 mole.

Enriched low-iron talc from the Alguiskoe deposit and enriched wollastonite from the Slyudyanskoe deposit (mineral content of 96 – 97%) were used in the experiments. The chemical composition of the minerals is shown in Table 1.

Finely pulverized minerals were mixed according to the composition of the initial batch mixtures (Table 2), and then oxides of calcium (in the form of $CaCO_3$) and magnesium and salts of coloring metals were added. The dried mixture was fired at temperatures of 1200 – 1300°C. The cake was ground to a residue no more than 2% on a No. 006 sieve. The pigments were tested as underglaze paints in painting of ma-

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TABLE 1

Mineral	Weight content, %							
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	P_2O_5	loss after calcination
Talc	63.00		0.89	0.06	0.14	31.53	–	4.70
Wollastonite	48.94	–	0.10	0.04	47.86	1.22	0.13	1.71

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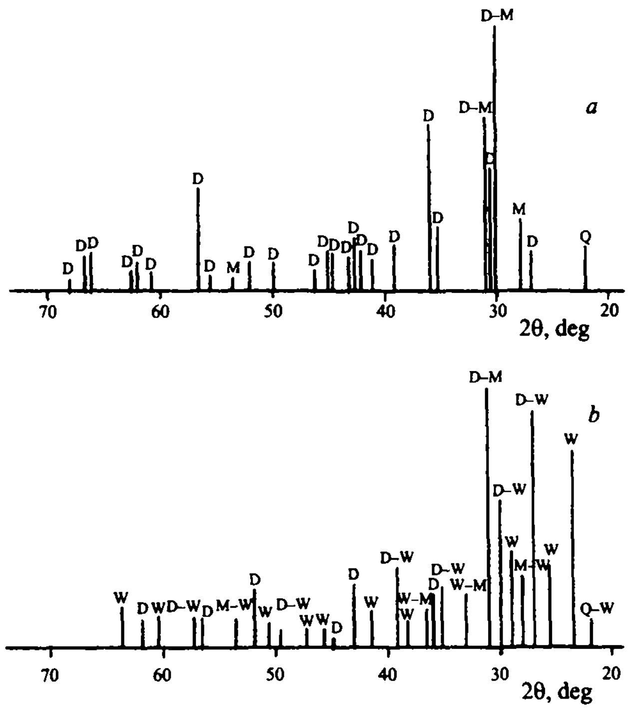

Fig. 1. X-ray patterns of blank tests (without chromophores) obtained from reactions 1 (*a*) and 2 (*b*). Firing temperature of 1200°C. Q) quartz, D) diopside; M) magnesium metasilicate; W) wollastonite.

TABLE 2

Pigment	Mole quantity MeO	Weight content, %								
		$CaSiO_3$	talc	CaO	MgO	Fe_2O_3	NiO	CuO	Cr_2O_3	CoO
D-1	0.5	32.30	52.59	3.90	–	11.10	–	–	–	–
D-2	1.0	30.13	49.15	–	–	20.72	–	–	–	–
D-3	0.5	34.33	56.00	4.14	–	–	5.52	–	–	–
D-4	1.0	33.87	55.24	–	–	–	10.90	–	–	–
D-5	0.5	32.48	52.98	3.92	–	–	–	–	10.63	–
D-6	1.0	30.44	49.56	–	–	–	–	–	19.92	–
D-7	0.5	34.33	55.99	4.14	–	–	–	–	–	5.54
D-8	1.0	33.86	55.22	–	–	–	–	–	–	10.92
D-9	0.5	49.23	40.17	–	2.14	8.46	–	–	–	–
D-10	1.0	46.30	37.77	–	–	15.92	–	–	–	–
D-11	0.5	51.55	42.06	–	2.24	–	4.15	–	–	–
D-12	1.0	50.59	41.27	–	–	–	8.14	–	–	–
D-13	0.5	51.42	41.95	–	2.23	–	–	4.40	–	–
D-14	1.0	50.32	41.06	–	–	–	–	8.62	–	–
D-15	0.5	49.43	40.33	–	2.15	–	–	–	8.09	–
D-16	1.0	46.66	38.07	–	–	–	–	–	15.27	–
D-17	0.5	51.55	42.06	–	2.24	–	–	–	–	4.16
D-18	1.0	50.58	41.26	–	–	–	–	–	–	8.16
KhP-1*	–	34.81	56.78	8.41	–	–	–	–	–	–
KhP-2*	–	52.56	42.88	–	4.56	–	–	–	–	–

* Blank test compositions obtained from reactions (1) and (2).

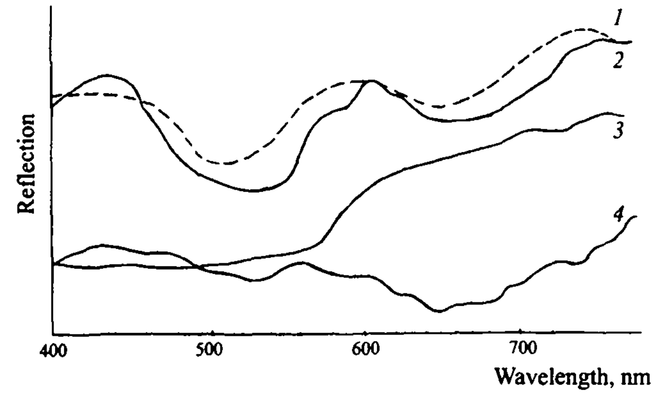

Fig. 2. Spectral curves of pigment reflection D-7 (*1*), D-18 (*2*), D-10 (*3*) and D-3 (*4*) Reflection Wavelength, nm.

jolica products. The color of the pigments and paints obtained is given in Table 3.

The radiographic analysis of the pigments obtained was carried out on DRON-3M unit. It was established that as a result of reaction (1), a clearly pronounced diopside structure is formed. $MgSiO_3$ and SiO_2 (Fig. 1) are present in small quantities. The reaction probably does not proceed to the end. CaO is the diffusing component in the reaction between the calcium oxide and silicon oxide emerging from decomposition of the talc [2]. It is known from the literature data that the primary products of the reaction in the CaO – SiO_2 system at temperature of 1200°C are, above all, Ca_2SiO_4 and also $Ca_3Si_2O_7$. The layer of these primary products resists diffusion, therefore the degree of transformation of SiO_2 is significantly lower than that of CaO. Moreover, the presence of other components impeding the course of reaction, as well as the possibility of their binding with calcium oxide, ought to be taken into account. However, on the whole, it can be stated that the main purpose of obtaining a diopside structure was successfully solved.

TABLE 3

Pigment	Color of pigment, firing temperature 1200°C	Color of subglaze, firing temperature 1050°C
D-1	Grey	Light brown
D-2	Dark gray	Brown
D-3	Light green	Light green
D-4	Lettuce-green	Lettuce-green
D-7	Light lilac	Light blue
D-8	Bright pink	Bluish-violet
D-10	Golden ocher-colored	Brown
D-12	Light yellow	Lettuce-green
D-14	Light turquoise	Turquoise
D-16	Light green	Grayish-green
D-18	Lilac	Bluish-violet

Addition of coloring oxides does not change the basic structure, and the coloring ions are incorporated well in the lattice.

As for reaction (2), the situation here is more complicated. In addition to diopside, a great number of peaks typical of wollastonite was identified. It can be assumed that magnesium oxide is not bound to the silicon oxide and remaining wollastonite, but primarily reacts with metasilicate, producing forsterite. As a consequence, wollastonite remains in excess. The literature data [2] also indicate that in the $MgO - SiO_2$ system at temperature of 1200°C out of three possible parallel reactions:

$$MgO \cdot SiO_2 + MgO = 2MgO \cdot SiO_2;$$

$$2MgO \cdot SiO_2 + SiO_2 = 2(MgO \cdot SiO_2);$$

$$MgO + SiO_2 = MgO \cdot SiO_2,$$

the rate of the first reaction is highest. Therefore, in the beginning of the process, the predominant formation of magnesium orthosilicate is observed. Only later on, after MgO binding, the residual silicon dioxide reacts to magnesium orthosilicate, producing $MgSiO_3$.

More components take part in reaction (2) than in reaction (1), therefore, the process of diopside structure formation is more complicated and is possibly shifted toward the area of higher temperatures than the ones investigated.

The general picture does not change with introduction of chromophoric oxides. Unusual behavior is exhibited only by ferrous and cuprous oxides. With a content of these oxides of 0.5 mole, the result is similar to that of other chromophores, and with 1 mole content, a purer diopside structure without inclusions of wollastonite is formed.

TABLE 4

Pigment*	Chromaticity coordinates		Wavelength, nm	Tint purity, %
	x	y		
D-3	0.29	0.30	480	10
D-7	0.34	0.32	507	3
D-10	0.41	0.35	600	32
D-18	0.34	0.30	530	7

* For D-7, D-18 additional wavelength, for D-3, D-10 predominant wavelength.

Spectrophotometric analysis was performed with a SF-10 spectrophotometer. Fig. 2 shows the pigment reflection curves, and Table 4 provides their color characteristics.

In conclusion, it should be added that talc is a fairly common mineral, therefore its application lowers the cost of ceramic pigment production and simplifies the technological process.

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